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THE MECHANISM AND KINETICS OF PLATFORMING
REACTIONS OF HYDROCARBONS.

PART IV ON THE DUAL PROPERTIES OF
PLATFORMING CATALYSTS

By Chang Yen-ch'ing
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- COMMUNIST CHINA -

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THE MECHANISM AND KINETICS OF PLAT-
FORMING REACTIONS OF HYDROCARBONS.
PART IV
ON THE DUAL PROPERTIES OF
PLATFORMING CATALYSTS*

- COMMUNIST CHINA -

Following is the translation of an article
entitled "The Mechanism and Kinetics of
Platforming Reactions of Hydrocarbons.
Part IV. On the Dual Properties of Plat-
forming Catalysts"* by Chang Yen-ch'ing
(1728 2518 3237) and I. V. Kalechits,
Institute of Petroleum, Academia Sinica,
in Jan-liao Hsueh-pao (Acta Focalia Sinica),
Vol. 4, No. 2, Shanghai, April 1959, pages
127-132.

Abstract

Hydrogenations are carried out with four kinds of isolated hydrocarbons, cyclohexane, cyclohexene, methylcyclopentane and methylcyclopentene, etc., by using three kinds of catalysts, Pt-Al₂O₃, HF-Al₂O₃, and Pt-HF-Al₂O₃. It is found that Pt-HF-Al₂O₃ is superior in its dehydrogenation, isomerization and isomerization-dehydrogenation, etc., properties than the other two types of catalysts. It is also found that both Pt-Al₂O₃ and HF-Al₂O₃ are not single function catalysts possessing either dehydrogenation or isomerization properties only, but dual function catalysts possessing poorer activities. When HF is added to Pt-Al₂O₃, or Pt is added to HF-Al₂O₃, the resulting catalysts are dual function catalysts with excellent activities. Based on these findings, we have assumed that active groups (or polyactive centers) are formed by Pt and HF on the surface

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of the catalyst. Moreover, based on this hypothesis and the results of experiments, we have proposed the transformation stages of aromatization of methylcyclopentane and, among these, the isomerization of methylcyclopentene is the slowest process.

Under the conditions adopted in most reforming processes, platforming catalysts, such as small amounts of Pt and HF supported on Al_2O_3 , possess good dehydrogenation and isomerization activities. They also show good cracking, coking properties and are less susceptible to poisoning, thus fairly satisfactory to industrial requirements. In connection with this type of catalyst, having dual properties, both metallic and acidic, and polyfunctional, the "Houdriforming" catalyst has been chosen by Mills, etc., in their study⁽¹⁾. Tests have also been carried out by Kuo Hsieh-hsien (6753 3610 6343), etc., of this institute on laboratory prepared platforming catalysts with isolated hydrocarbons, such as methylcyclohexane, methylcyclopentane, n-heptane, etc., as starting materials and the assumption concerning the reaction mechanism and the dual activity centers of catalysts has been made⁽²⁾. However, the present available information related to this complicated and important problem is far from sufficient. Consequently, in order to gain an insight into the functions of Pt and HF in the catalysts and the transformation mechanism in the aromatization of certain cyclic paraffinic hydrocarbons, such as methylcyclopentane and cyclohexane with platforming catalysts, three kinds of catalysts have been prepared, Pt- Al_2O_3 , HF- Al_2O_3 , HF-Pt- Al_2O_3 . Four kinds of isolated hydrocarbons, such as methylcyclopentane, methylcyclopentene, cyclohexane, cyclohexene and a mixture of cyclopentane and cyclohexane (1:1) are used in the investigation of reactions occurring with these catalysts.

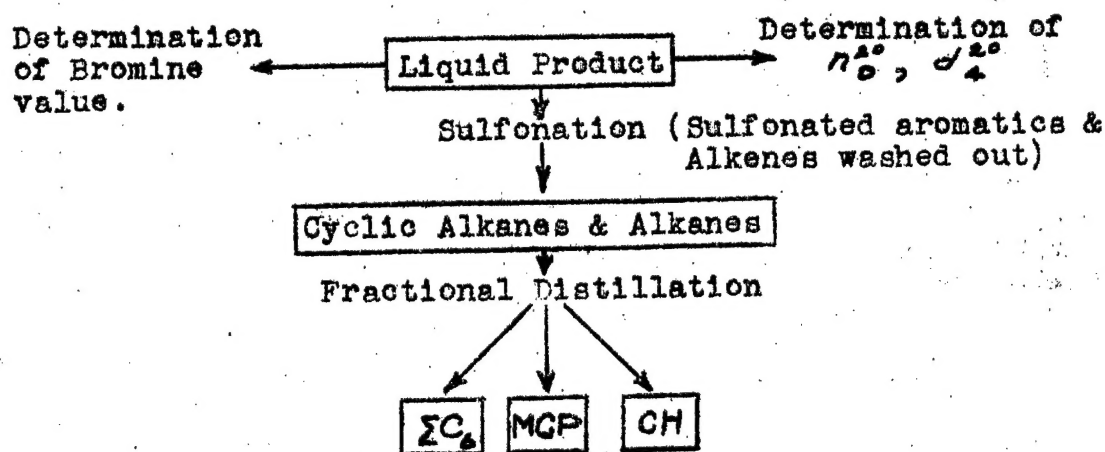
Experimental

Catalysts used; Pt- Al_2O_3 , containing 0.3% Pt. and HF- Al_2O_3 , containing 1.5% HF. These were the catalysts used in platforming.

Starting material, isolated hydrocarbons; cyclohexane, b.p. 80-81°, refractive index of $n_D^{20} = 1.4262$, sp. gr. $d_4^{20} = 0.7785$; methylcyclopentane, b.p. 71-72°, refractive index of $n_D^{20} = 1.4100$, sp. gr. $d_4^{20} = 0.7482$; methylcyclopentene, b.p. 64-68° and 74.8-77.8°, all of its three isomers being present, refractive index of $n_D^{20} = 1.4267$, sp. gr. $d_4^{20} = 0.7701$; cyclopentene, b.p. 82-83°, refractive index of $n_D^{20} = 1.4460$, sp. gr. $d_4^{20} = 0.800$. Methylcyclopentane, methylcyclopentene and cyclohexene were all laboratory prepared.

Reaction conditions; temperature 430°, pressure 20 atms., space velocity 3.0 volume per volume per hour, mole ratio of hydrogen to hydrocarbon 6:1.

The methods used for product analysis were similar to those employed in analyzing the products of methylcyclopentane and cyclohexane when these were used as starting materials and the methods described in Part II and Part III of this project. The products obtained from methylcyclopentene and cyclohexene were analyzed according to the following scheme.

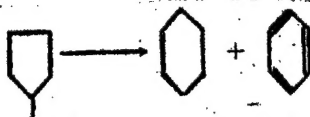


Results. The results obtained were tabulated in table 1: Reforming Results of Hydrocarbons Using Three Kinds of Catalysts.

Starting Material	Catalyst	% Weight (Vs. Product)				
		Aromatics	Alkenes	C ₆ Hydrocarbons	Methylcyclopentane	Cyclohexane
Methylcyclopentane	HF-Al ₂ O ₃	0.24	—	0.0	92.8—98.8	5.0—7.0
	Pt-Al ₂ O ₃	1.00	—	1.8	91.0	0.0
	Pt-HF-Al ₂ O ₃	14.1	—	5.8	79.0	7.1
Methylcyclopentene	HF-Al ₂ O ₃	9.2	87.0	0.7	59.1	0.0
	Pt-Al ₂ O ₃	5.3	1.0	0.0	91.8	2.4
	Pt-HF-Al ₂ O ₃	18.8	0.3	7.8	57.2	16.2
Cyclohexane	HF-Al ₂ O ₃	0.8	—	0.0	0.0	99.2
	Pt-Al ₂ O ₃	30.5	—	0.0	0.0	63.5
	Pt-HF-Al ₂ O ₃	71.0	—	0.0	18.8	10.7
Cyclohexene	HF-Al ₂ O ₃	31.8	27.7	0.7	26.8	13.5
	Pt-Al ₂ O ₃	49.7	0.8	0.0	18.5	30.8
	Pt-HF-Al ₂ O ₃	72.8	0.1	0.7	17.9	8.5
Methylcyclopentene + cyclohexene (1:1)	HF-Al ₂ O ₃	0.4	—	0.0	47.4	52.2
	Pt-Al ₂ O ₃	18.8	—	0.0	51.0	30.2
	Pt-HF-Al ₂ O ₃	40.2	—	12.1	44.6	3.1

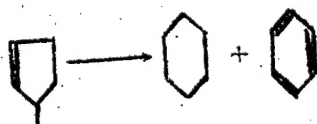
Discussion

(1) Isomerization of methylcyclopentane occurs slightly when HF-Al₂O₃ and Pt-Al₂O₃ are used, but more extensively by using Pt-HF-Al₂O₃. For example, the formation of cyclohexane and aromatics by isomerizing methylcyclopentane:



The extent of isomerization is using HF-Al₂O₃ is 7.2% and 1.0% in the case of Pt-Al₂O₃ but, 21.2% when Pt-HF-Al₂O₃ is employed.

Similar results are obtained in isomerizing methylcyclopentene, i.e., reaction is small when using HF-Al₂O₃ and Pt-Al₂O₃, but more intense in the case of Pt-HF-Al₂O₃. For example, the formation of cyclohexane and aromatics by isomerizing methylcyclopentene:



The rate of isomerization is 9.2% using HF-Al₂O₃, 7.7% with Pt-Al₂O₃, and 35.0% in the case of Pt-HF-Al₂O₃.

Basically, the isomerization of cyclohexane with the formation of methylcyclopentane does not take place by the use of HF-Al₂O₃, or Pt-Al₂O₃. However, when Pt-HF-Al₂O₃ is used, the methylcyclopentane formed in the products reached 18.3%.

These results show that the isomerization properties of either HF-Al₂O₃ or Pt-Al₂O₃ are poor and that Pt-HF-Al₂O₃ possesses prominent isomerization properties.

(2) The dehydrogenation of cyclohexane forming benzene basically does not take place when HF-Al₂O₃ is used, and only to a small extent, 36.5%, by using Pt-Al₂O₃. However, dehydrogenation takes place readily in the presence of Pt-HF-Al₂O₃ and the aromatics formed reach 71.0%.

Similar results have been observed in the formation of benzene by the dehydrogenation of cyclohexene. Aromatics formed using HF-Al₂O₃ amount to 31.3% and for Pt-Al₂O₃, 49.7%, but they reach 72.8% in the case of Pt-HF-Al₂O₃.

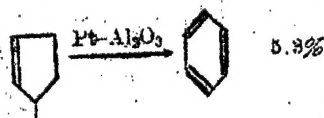
These results show that both HF-Al₂O₃ and Pt-Al₂O₃ are poor in their dehydrogenation properties and only Pt-HF-Al₂O₃ is outstanding in this respect.

(3) The isomerization, dehydrogenation of methylcyclopentane and methylcyclopentene with the formation of

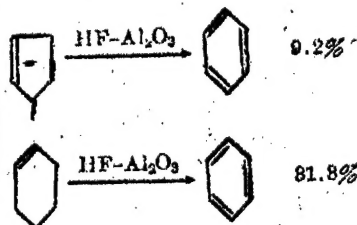
benzene are more or less similar to the above results. That is, little reaction takes place with either $\text{HF-Al}_2\text{O}_3$ or $\text{Pt-Al}_2\text{O}_3$ and the reaction is more intense in the case of $\text{Pt-HF-Al}_2\text{O}_3$. Thus, it is shown that $\text{Pt-HF-Al}_2\text{O}_3$ is a new, polyfunction catalyst.

According to the above three points, $\text{Pt-HF-Al}_2\text{O}_3$ as a catalyst is far superior to the properties of either $\text{Pt-Al}_2\text{O}_3$ or $\text{HF-Al}_2\text{O}_3$, or a mechanical mixture of these two, whether in isomerization, dehydrogenation or isomerization-dehydrogenation, etc.

(4) Either $\text{Pt-Al}_2\text{O}_3$ or $\text{HF-Al}_2\text{O}_3$ are not strictly single function catalysts. For example, when $\text{Pt-Al}_2\text{O}_3$ is used in the following reaction, besides dehydrogenation, a small extent of isomerization also takes place with the formation of benzene, e.g.,



When $\text{HF-Al}_2\text{O}_3$ is used, besides the isomerization reaction, some dehydrogenation takes place, e.g.,



Although both $\text{HF-Al}_2\text{O}_3$ and $\text{Pt-Al}_2\text{O}_3$ possess dehydrogenation and isomerization properties, they are dual function catalysts poor in these properties. If a small amount of Pt is added to $\text{HF-Al}_2\text{O}_3$ or if HF is added to $\text{Pt-Al}_2\text{O}_3$, then both of them become polyfunctional catalysts with good isomerization and dehydrogenation properties.

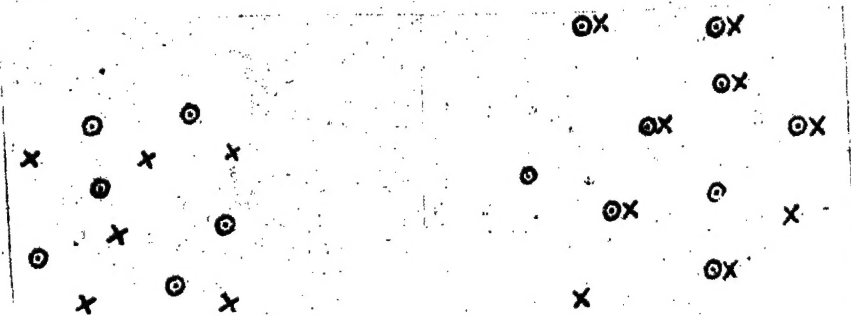
Based on the above points, we set forth our hypothesis regarding polyactive centers (or polyfunctional active groups) of platforming catalysts as follows.

The Pt and HF in $\text{Pt-HF-Al}_2\text{O}_3$ are distributed on the surface of $\text{Pt-HF-Al}_2\text{O}_3$, not without being interrelated, but forming active groups. These active groups possess excellent catalytic properties upon which the isomerization, dehydrogenation, isomerization-dehydrogenation, hydrogenolysis, etc., of hydrocarbons are mainly carried out. Within these groups the dehydrogenation activity of Pt and the isomerization property of HF are greatly enhanced by the presence of each other. The surface of the catalyst may contain

ungrouped Pt and HF, both of which possess weak dehydrogenation and isomerization properties just like the Pt in Pt-Al₂O₃ and the HF in HF-Al₂O₃, playing a minor role in catalysis.

The dehydrogenation taking place on the activity groups is still mainly attributed to the effects exerted by Pt. Similarly, isomerization occurs under the influence of HF (3).

The dual activity centers theory of platforming catalysts as suggested by Mills, Heinemann, etc. (1), differs in nature from our conception. First of all, they assumed that the Pt and HF are distributed on the surface of platforming catalysts without any interrelationship. The difference of the two assumptions is illustrated below.



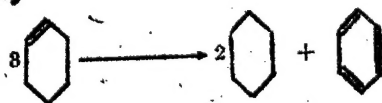
Mills, Heinemann, etc.

Author

Illustrations Showing Activity Centers

⊙ represents Pt; X represents HF; ⊙X represents the activity group.

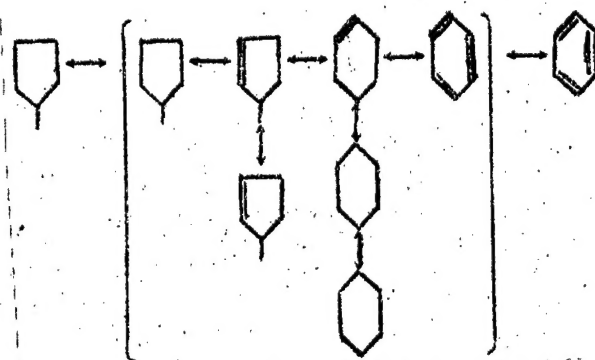
Secondly, their interpretations of HF-Al₂O₃ and Pt-Al₂O₃ are mechanical, i.e., HF-Al₂O₃ is a single function catalyst having only isomerization and no dehydrogenation properties and Pt-Al₂O₃ is also a single function catalyst having only dehydrogenation, but without isomerization properties. The isomerization properties of Pt-Al₂O₃, as explained by them, is caused by the residual acid in the catalyst, not washed out in the course of its preparation. Their explanation for the formation of benzene by the catalytic action of HF-Al₂O₃ on cyclohexene and methylcyclopentene is due to hydrogen transfer reaction attributed to the catalyst, rather than its dehydrogenation properties. This explanation is difficult to confirm by our results because if benzene is formed by the hydrogen transfer reaction,



then the ratio of benzene to cyclohexane in the product should be 1:2. However, the amount of cyclohexane obtained in our product is far less than the amount obtainable in the hydrogen transfer reaction.

The question of the mechanism of the aromatization of methylcyclopentane is discussed below.

According to Mills, Heinemann, etc., and Gonikberg (4), the reversible isomerization between methylcyclopentane and cyclohexane under the influence of the usual acidic or metallic catalysts is a transition stage of dehydrogenation-isomerization, i.e., isomerization follows the dehydrogenation stage. We agree with them on this point. Furthermore, our findings show that little cyclohexane is formed by the isomerization of methylcyclopentane using $\text{HF-Al}_2\text{O}_3$, and cyclohexane does not undergo isomerization when $\text{HF-Al}_2\text{O}_3$ is used. However, aromatics resulting from the isomerization of methylcyclopentane under the influence of $\text{HF-Al}_2\text{O}_3$ and the methylcyclopentene formed by the isomerization of cyclohexene using $\text{HF-Al}_2\text{O}_3$ are comparatively more substantial. These facts all serve as minor evidences showing that the dehydrogenation precedes isomerization. Based on this point and the assumption of the activity groups mentioned above, our proposal on the aromatization mechanism of methylcyclopentane using platforming catalysts is as follows:

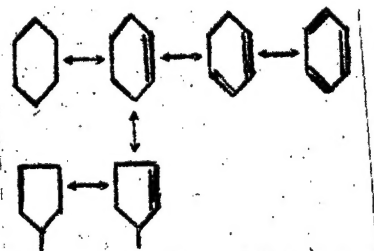


Reactions within the brackets are carried out on the activity groups situated on the surface of the catalyst. The reactions outside of the brackets take place in the gaseous phase.

According to the above illustrated transformation stages, a greater amount of aromatics should be formed if the intermediates of the later stages, methylcyclopentene and cyclohexene, are used as starting materials than if the intermediates of the first stages, methylcyclopentane, is used. The results obtained are in accord with this deduction: methylcyclopentane, methylcyclopentene and

cyclohexene were reacted separately using Pt-HF-Al₂O₃ and it was found that the benzene formation was in the increasing order of 14.1%, 18.8%, 72.8% in each case. When Pt-Al₂O₃ was used, the benzene formed was 1.0%, 5.3%, 49.7%. When HF-Al₂O₃ was used, the benzene formed was 0.2%, 9.2%, 31.3%. It is clearly shown by the above results that in the fore-mentioned transformation stages, the isomerization of methylcyclopentene with the formation of cyclohexene is the most difficult stage to be brought about and kept under control. This is due to the fact that the rate of benzene formation when cyclohexene is used as a starting material greatly exceeds that prevailing when methylcyclopentene or methylcyclopentane are used. Thus, it is clear that benzene forms readily after the isomerization stage.

According to the dual centers assumption proposed by Mills, Heinemann, etc., the mechanism for the formation of benzene by isomerization, dehydrogenation of methylcyclopentane or the dehydrogenation of cyclohexane is illustrated below.



The vertical reactions take place on the isomerization centers and the horizontal reactions take place on the dehydrogenation centers. In other words, methylcyclopentane is first adsorbed on the dehydrogenation center forming methylcyclopentene. The latter is then transferred to the isomerization center and converted to cyclohexene which is again transferred to the dehydrogenation center whereupon benzene is formed by stepwise dehydrogenation. It is thought that such numerous repeated transfers of the intermediates between the two kinds of activity centers would slow down the rate of reaction. However, in fact, the rate of aromatization proceeds briskly. At the same time, such repeated transfers between the activity centers would also be accompanied by the repeated process of detachment and adsorption. Thus, intermediates such as methylcyclopentene or cyclohexene would be found in the products. However, no such hydrocarbons have been isolated from our experiments. Although the reaction mechanism proposed by us also involves dehydrogenation, isomerization, etc., stages, these reactions all take place on the same

activity groups in a very convenient manner. And the intermediates forge steps of desorption and readsorption on the surface of the catalyst. Therefore, our mechanism should correspond more closely to the experimental results than the one proposed by Mills, Heinemann, etc.

Conclusion

1. Hydrogenation is carried out with four kinds of isolated hydrocarbons, methylcyclopentane, methylcyclopentene, cyclohexane and cyclohexene, etc., by using three kinds of catalysts, $\text{HF-Al}_2\text{O}_3$, $\text{Pt-Al}_2\text{O}_3$, and $\text{Pt-HF-Al}_2\text{O}_3$. It is found that $\text{Pt-HF-Al}_2\text{O}_3$ is superior in its dehydrogenation, isomerization and isomerization-dehydrogenation, etc., properties than the other two types of catalysts.

2. It is also found that both $\text{Pt-Al}_2\text{O}_3$, and $\text{HF-Al}_2\text{O}_3$ are not strictly single function catalysts, but dual function catalysts possessing poorer activities. When HF is added to $\text{Pt-Al}_2\text{O}_3$ or Pt is added to $\text{HF-Al}_2\text{O}_3$, the resulting catalysts are dual functional with excellent properties.

3. The assumption was proposed that Pt and HF may form active groups (or polyfunctional active centers) on the surface of platforming catalysts.

4. Suggestions were made concerning the transformation stages of the aromatization of methylcyclopentane under platforming conditions. Among these stages, the isomerization of methylcyclopentene forming cyclohexene is the slowest.

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